organic solvents and were discarded. The mother liquor was successively extracted with light petrol and $CHCl_3$ (to remove the mixture of triperpenoid acetates and cinnamates). The aqueous phase was diluted with EtOH and stirred with freshly prepared PbO to precipitate tannins. The process was repeated until the filtrate gave no positive test for phenols [3]. The clear filtrate was concentrated (to 600 cm^3) and successively extracted [2] with $CHCl_3$, $CHCl_3$–EtOH (2:1), and $CHCl_3$–EtOH (3:2) to give on removal of solvents thick syrups (2 g, 16 g and 3.5 g respectively). Each of the extracts showed the presence of cardiac glycosides by the Kedde test [9]. TLC [10] silica gel of a sample of the $CHCl_3$–EtOH (2:1) extract indicated the presence of cardiac glycosides and amino acid betaines. This extract gave two crystalline betaines I and II on fractional crystallisation from cold Me_2CO–MeOH. The mother liquor obtained after crystallisation of the betaines contained mainly cardiac glycosides [11].

Betaine I was recrystallised from methanol and had mp 270–274°. It analyses for $C_{14}H_{18}N_2O_2$. IR, 3200–2600; 1620 (C=O); 750 (aromatic ring). NMR of betaine I (D_2O, TMS external reference) showed the presence of five aromatic protons at 7.10–7.65 (5 H, *m*), a one proton multiplet around 4.1 (1 H, *m*), a two proton doublet around 3.2 (2 H, *d*, *J* 6 Hz) one arm of which was together with a ten-proton singlet at 3.1 (10 H, *s*, $-N^+(Me)_3$). It formed a nitrate (aq MeOH soln acidified with 4*M* HNO_3) mp 220–230° (decomposition), $C_{14}H_{19}N_3O_5$; a HCl-ide $C_{14}H_{19}N_2O_2Cl$, softened at 240° and decomposed at 253–255°. Betaine I was identical mp IR, NMR with tryptophan betaine, synthesised [12] from (±)-tryptophan. Betaine II on recrystallisation from Me_2CO–MeOH had mp 240–242° (decomposition). It analysed for $C_{12}H_{17}NO_2$. IR, 3350, 2380; 1660 (C=O), 1600, 725, 710 and 680 (aromatic ring). NMR (D_2O, TMS external reference), 7.30 (5 H, *s*, aromatic protons), 3.8 (1 H, *m*, –CH–), 3.25 (10 H, *s*, $-N^+(Me)_3$), 3.15 (2 H, *d*, *J* 10 Hz, one arm of this doublet overshadowed by the $-N^+(Me)_3$ absorption at 3.25). Betaine II formed a HCl-ide, $C_{12}H_{18}NO_2Cl$, mp 220–224° and easily eliminated trimethylamine to form cinnamic acid on reflux with aqueous NaOH. Betaine II was identical mp IR, NMR with a sample of α-trimethyl-β-phenylpropiobetaine (phenylalanine betaine) synthesised by a modification of the method of Billman and Berg [13]. In this regard, phenylalanine was permethylated [12] in the cold with MeI and the required betaine was generated from the methiodide with aquous Ag_2SO_4 instead of Ag_2O. The bark of *A. africana* was also extracted with light petroleum to give a mixture of triterpene derivatives as found in the latex and with 95% EtOH which extracted a mixture of cardiac glycosides [11] and betaines similar to the extract of the latex. *Significance*: Triterpenoids and betaines are reported for the first time as constituents of the latex and bark of *A. africana* and the genus *Antiaris*. The latex is a good source of butyrospermol which was first isolated from shea butter [14] but has since been rather difficult to obtain in good quantity from that or any other readily available source. The co-occurrence of the cinnamic acid group and phenylalanine betaine in *A. africana* is of biogenetic significance.

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7-HYDROXYHEDYCHENONE, A FURANODITERPENE FROM *HEDYCHIUM SPICATUM**

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Key Word Index—*Hedychium spicatum*; Zingiberaceae; 7-hydroxyhedychenone; diterpene.

In continuation of earlier work on the furanoid diterpenes of *Hedychium spicatum* rhizomes [1], work-up of a larger quantity of rhizomes has yielded a second furanoditerpene, designated as 7-hydroxyhedychenone (13-β-furanolabda-6-keto-7,11-dien-7-ol; **1**). 7-Hydroxyhedychenone, white needles (hexane) mp 108–9°, $[\alpha]_D$ +125°, analyzed for $C_{20}H_{26}O_3$ (M^+ 314). It gave a positive Ehrlich test suggesting that it was a furanoid diterpene. This conclusion was substantiated by spectroscopic data. It had λ_{max} 215 (ε 12960), 230 (14510) and 278 nm (14200) suggesting possibly a conjugated furan and an α,β-unsaturated ketone. IR: (ν_{max} 3400 cm^{-1}), intramolecular bonded hydroxyl [2]; 1656 and 1642 cm^{-1}, α,β-unsaturated ketone; 1500 and 873 cm^{-1}, furan ring; and 970 cm^{-1}, *trans* olefinic double bond.

The NMR spectrum showed a furan ring Hs (2·57 τ, *m*, 2α-H and 3·44 *m*, 1β-H); three quaternary C-CH_3 (9·02, 8·82 and 8·79) and a CH_3 on a double bond (*d*, 8·2, *J* 2 Hz). No resonance was attributable to >CHOH, showing a tertiary OH which gives a singlet at 6·7 in

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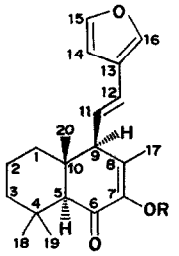
DMSO [3] and a broad hump at 4·7 in $CDCl_3$ which disappears in D_2O. The signal of a methine H 7·8(s) and at 7·02 (*q*, *J* 1·3 Hz and *d*, *J* 10 Hz). *Trans* coupling of the two olefinic H is suggested as they resonate as doublets at 3·57 (*J* 16 Hz) and 4·24 (*J* 16 Hz).

The MS had peaks at *m/e* 81 and 93 formed through fission [4] of C11-C12 and C9-C11 bonds with rearrangement and H transfer suggesting that the furan ring was attached through a conjugated double bond to the rest of the molecule. The base peak *m/e* 190, presumably formed through a retro-Diels–Alder type cleavage, located the OH group in ring B. The fact that ring A has no oxygen substituents, is shown by intense peaks at *m/e* 123 and *m/e* 109. Ion *m/e* 123 also provided evidence for the location of the keto function at C-6 (**1**). The ion *m/e* 93 was replaced in the spectrum of the dihydro product by one at 95. The reduction of the side chain double bond (11–12) in this compound was confirmed by the UV, λ_{max} 220 nm (5530) and 279 nm (6863). The newly formed methylene H gave rise to NMR signal at 7·89 and 6·2. The chemical shift of the CH_3 on the ring double bond remained unchanged at 8·1τ.

The IR spectrum of the monoacetate had C=O stretching at 1755 cm^{-1} indicating the OH was an enol. This was supported by a UV data of 7-hydroxyhedychenone acetate [λ_{max} 217 nm (8644) and 241 nm (13430)].

The location of a CO function at C-6 received support from its complete inertness [5]. LAH reduction yielded a product having λ_{max} 210 nm (12300) and 232 nm (14160) and ν_{max} 1712 cm^{-1} indicating the reduction of the enone double bond (7,8) but not of the ketone function. The NMR spectrum of this compound showed the C-8 CH_3 signals as a doublet at 8·75 (*d*, *J* 7 Hz) and for CHOH at 6·4 (*dm*, *J* 9 Hz). The coupling constant (9 Hz) indicated that the C-7 and C-8 H are *trans* diaxial. The inertness of the 6-keto function in 7-hydroxyhedychenone can be ascribed to steric hindrance of substituents located 1,3 with respect to C-6. These are the axial C-19β and C-20β and C-18α Me [6].



(**1**) R = H
(**2**) R = Ac

The chemical shifts of C-20 CH_3 in the NMR spectra of 7-hydroxyhedychenone, dihydro-7-hydroxyhedychenone and 7-hydroxyhedychanone are 9·02, 9·17 and 9·05 respectively and suggest that the C-20 Me and C-9(11) bond are *cis*. The dextrorotation 7-hydroxyhedychenone and its derivatives suggests β-stereochemistry [1] at C-9 and C-10 as in (**1**). The structure of 7-hydroxyhedychenone can, therefore, be represented by 13β-furanolabda-6-keto-7,11-dien-7-ol (**1**). The stereochemical assignments being tentative.

EXPERIMENTAL

Uncorrected capillary mp and photoelectrically measured $[\alpha]_D$ in $CHCl_3$ are reported. IR, UV and 60 Mcs NMR spectra were determined in KBr, MeOH and $CDCl_3$ with TMS as internal standard unless indicated. TLC were done on SiO_2 plates.

Isolation of 7-hydroxyhedychenone (**1**). Dried and milled rhizomes of *H. spicatum* (13 kg) were extracted with 50% EtOH by cold percolation and the extract concd. under red. pres. to 1/10 vol. This concentrate was diluted with an equal vol. H_2O and extracted successively with C_6H_{14}, C_6H_6, EtOAc (3 × 2 l. each). Of the C_6H_6 soluble fraction (130 g) 80 g was chromatographed on silica (1·5 kg). Elution with C_6H_{14}, C_6H_{14}–C_6H_6 (1:1), C_6H_6 and EtOAc yielded the mixture of hedychenone and 7-hydroxyhedychenone (2 g) from C_6H_{14}–C_6H_6 (1:1) eluate. The mixture was further chromatographed over basic alumina (80 g). Elution with C_6H_{14}, C_6H_{14}–C_6H_6, C_6H_6 and EtOAc yielded 7-hydroxyhedychenone (150 mg) from C_6H_6–EtOAc (1:1) eluate. It crystallized as needles from C_6H_{14} in cold mp 108–9°. $[\alpha]_D$ +125°. (Found: C, 76·81; H, 8·02. $C_{20}H_{26}O_3$ requires C, 76·43; H, 8·28%).

Acetylation of 7-hydroxyhedychenone (**2**). Acetylation of 1 with C_5H_5N–Ac_2O overnight and purification by preparative TLC gave a monoacetate which did not crystallize; M^+ 356; ν_{max} (neat) 2900, 1755, 1677, 1420, 1360, 1225, 1050, 1028, 873 and 760 cm^{-1}; NMR (CCl_4): τ 8·95, 8·86, 8·83 (3*s* 9H), 8·3 (*d* 3H, *J* 1·5 Hz), 7·85 (*s* 1H), 7·8 (*s* 3H), 6·95 (*dm* 1H, *J* 10 Hz), 4·26 (*dq* 1H, *J* 16 and 10 Hz), 3·62 (*d* 1H, *J* 16 Hz), 3·5 (*bs* 1H) and 2·64 (*m* 2H). (Found: C, 74·30; H, 8·10. $C_{22}H_{28}O_4$ requires C, 74·16; H, 7·87%).

Dihydro-7-hydroxyhedychenone. 1 (55 mg) was hydrogenated in presence of Pd–C (10%) in EtOH for 1 hr. Filtration and removal of solvent gave the oily product, which was purified by preparative TLC; $[\alpha]_D$ +0·7°; ν_{max} (neat) 3401, 2907, 1669, 1647, 1471, 1383, 1362, 1326, 1297, 1199, 1168, 1148, 1124, 1052, 1028, 923 and 879 cm^{-1}. NMR; τ 9·17, 8·87, 8·8 (3*s* 9H), 8·1 (*d* 3H, *J* 1·5 Hz), 7·89 (*bs* 2H), 7·85 (*s* 1H), 6·63 (*dq* 1H, *J* 9 and 2 Hz), 6·2 (*m* 2H), 3·72 (*m* 1H) and 2·67 (*m* 2H). MS (*m/e*): 316 (M^+), 301, 234, 193, 191, 165, 151, 149, 135, 123, 109, 95, 85, 83 (base peak), 81, 71, 69, 57 and 55. (Found: C, 75·54; H, 8·80. $C_{20}H_{28}O_3$ requires C, 75·94; H, 8·86%).

7-Hydroxyhedychanone. LAH (*ca* 150 mg) was added to a stirred solution of 1 in dry THF (30 ml) at 0°. After stirring for further 4 hr, excess LAH was decomposed with EtOAc, the reaction mixture treated with dil. H_2SO_4 and the product extracted with Et_2O. The major product was isolated by preparative TLC as an oil (4); M^+ 316; $[\alpha]_D$ +44°; ν_{max} (neat) 2460, 2907, 1712, 1462, 1391, 1366, 1292, 1264, 1244, 1164, 1104, 1075, 1043, 1027, 973, 944, 920 and 876 cm^{-1}. NMR (CCl_4): τ 9·15, 9·05, 8·83 (3*s* 9H), 8·75 (*d* 3H, *J* 7 Hz), 8·83 (*m* 6H), 6·84 (broad hump 1H), 6·4 (*dm* 1H, *J* 9 Hz), 4·5 (*dq* 1H, *J* 16 and 9 Hz), 3·73 (*d* 1H, *J* 16 Hz), 3·59 (*m* 1H) and 2·7 (*bs* 2H). (Found: C, 75·46; H, 8·83. $C_{20}H_{28}O_3$ requires C, 75·94; H, 8·86%).

Acetylation of 7-hydroxyhedychanone. 4 (40 mg) was allowed to stand with C_5H_5N–Ac_2O overnight and purified by preparative TLC. The required acetate was obtained as an oil; ν_{max} (neat) 2865, 1742, 1727, 1464, 1391, 1375, 1267, 1241, 1153, 1032, 977, 876 and 785 cm^{-1}. NMR: τ 9·11, 9·07 (2*s* 6H), 8·73 (*s* 6H), 7·83 (*s* 3H), 5·39 (*dm* 1H, *J* 10 Hz), 4·33 (*dq* 1H, *J* 11 Hz), 3·67 (*d* 1H, *J* 16 Hz), 3·5 (*m* 1H) and 2·63 (*m* 2H). (Found: C, 73·94; H, 8·51. $C_{22}H_{30}O_4$ requires C, 73·74; H, 8·38%).

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